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DIFFUSION PROCESSES IN LEAD-SILICATE GLASSES IN GAS HEAT TREATMENT WITH NITROGEN

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The character of diffusion of oxygen and nitrogen in the surface layer of nitrated lead-silicate glass was investigated. The dependences of the diffusion coefficients on the composition of the glass and duration of gas heat treatment were established.

The basis of modification of the surface of glass (ion exchange, doping, application of coatings, spraying glass of another composition) is diffusion, i.e., the microscopic motion of ions that causes macroscopic alterations in the structure (composition) of the glass. The mechanism of diffusion and its correlation with the structure and physicochemical properties of glass have been investigated in many studies [1 – 4]. These investigators believe that only cations are capable of diffusion in glass. However, the analysis of the published data in [5] concerning the effect of nitrogen-containing gases on the surface of glasses indicates that the mechanism of their reaction consists of a change in the anion composition of the surface layer of the glass — substitution of three oxygen ions by two nitrogen ions, i.e., reciprocal anion diffusion $3O^{2-} \rightleftarrows 2N^{3-}$ takes place. Substitution of two-coordinated oxygen by three-coordinated nitrogen increases the degree of coherence of the structural skeleton and "shrinkage" of the structure due to formation of cross links between elemental oxygen chains and the more covalent nature of nitrogen in comparison to oxygen [5].

We investigated optical lead-silicate glasses TF-1 ($69SiO_2 \cdot 23PbO \cdot 8K_2O$),[2] TF-5 ($61SiO_2 \cdot 35PbO \cdot 4K_2O$), TF-10 [$58SiO_2 \cdot 40PbO \cdot 2(K_2O + Na_2O)$]. The glass samples underwent gas heat treatment with nitrogen at a temperature of 425°C and pressure of 1 MPa for 5 – 20 h. The diffusion coefficient of oxygen and nitrogen in the modified upper layer of the glasses was then determined.

The existing methods of measuring the diffusion coefficient (sectioning method, grinding, absorption method, etc.) [5] are not applicable in the given case due to the low concentrations of oxygen and nitrogen that participate in the diffusion process [6]. For this reason, we determined the diffusion coefficient with the results of Auger spectroscopy, one of the most sensitive methods of analyzing the quantitative composition of the surface of glass. The spectra were obtained with a LAS-3000 electron-ion spectrometer. The samples were irradiated with an electron beam with energy of approximately 3 keV. The measuring instrument operated in the mode of recording the $N^{2-}(E)$ secondary electron derivative. The profiles of the concentrations of elements in the surface layer of the glass were obtained by ion etching — removal (sputtering) of the target material by layers in bombardment with high-energy ions (in the given case, Ar^+ ions with 3 keV energy) followed by an analysis of the surface formed. The sputtering rate was approximately 10 nm/min. The quantitative analysis was conducted by the elemental sensitivity factor method [7].

The nitrogen and oxygen diffusion coefficients were determined by the Boltzmann–Matano method [8]. The calculation was performed with the equation:

$$\tilde{D}(C) = -\frac{1}{2t}\frac{dx}{dC}\int_0^C x\,dC,$$

where t is the duration of the gas heat treatment, sec; x is the layer depth, nm; C is the proportion of diffusing ions; $C = (1 - c_h/c_0) \cdot 100$ (c_0 and c_h are the atomic ion content in the glass before and after gas heat treatment, %).

The analysis of the element concentration profiles in the surface layer of the nitrated glass (Fig. 1) indicates the mutually reversible character of the oxygen and nitrogen distribution. The concentration profiles of the other elements (silicon, lead, and potassium) in the nitrated and initial glasses were almost the same.

The presence of carbon in the surface layer is caused by absorption and subsequent reaction of the alkaline components of the glass and atmospheric carbon dioxide with formation of carbonates during mechanical treatment of the glass [7].

A comparison of the data obtained and the published data serves as direct experimental evidence that together with in-

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[2] Here and below, if not explicitly stated otherwise, molar content.

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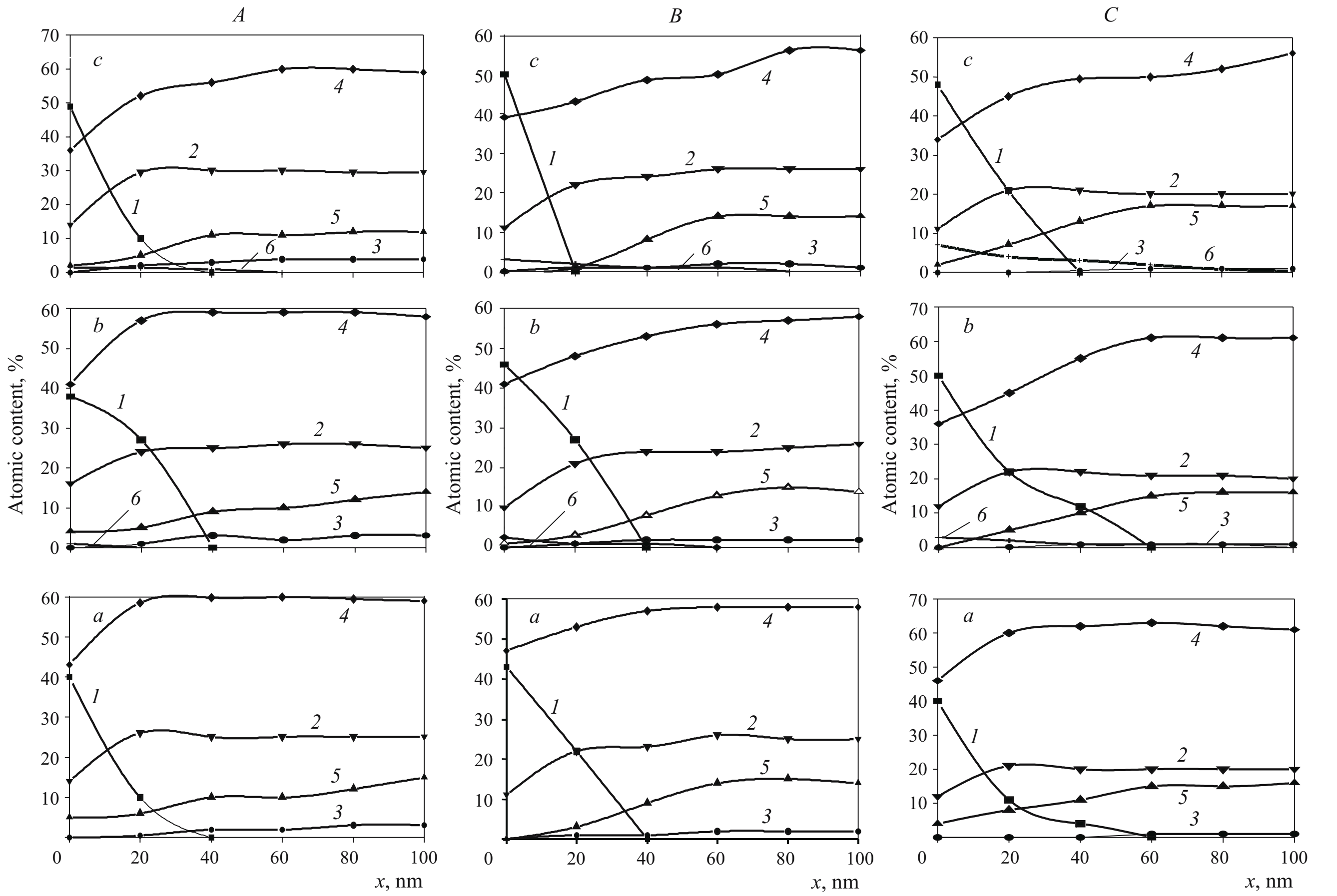

Fig. 1. Profiles of the concentrations of elements in the surface layer of TF-1 (*A*), TF-5 (*B*), and TF-10 (*C*) glasses: *a*) initial glass; *b* and *c*) after nitration at 425°C and 1 MPa for 5 and 20 h; *1*) C; *2*) Si; *3*) K; *4*) O; *5*) Pb; *6*) N.

troduction of molecules of nitrogen in the surface of the glass [6], divalent oxygen is substituted by trivalent nitrogen. The diffusion process in this case has prerequisites, since oxygen and nitrogen ions (as neighboring with respect to group in the periodic table) differ insignificantly in ionic radii, polarizability, and charge value.

The analysis of the experimental data (Fig. 2) shows that the diffusion coefficients of oxygen and nitrogen ions are insignificant in comparison to the cation diffusion coefficients. However, in the series of glasses TF-1, TF-5, and TF-10, i.e., with an increase in the lead oxide content in them, the diffusion coefficients also increase. This is in particular due to the bond strength of the ions in the polyhedron, since in diffusion the ion should execute a diffusion jump after overcoming the potential barrier. Lead-silicate glass of the investigated compositions has the entire spectrum of potential barriers or bond energies [9]. The Si – O bond energy (i.e., strength of attachment of oxygen) predominates.

Type of bond	Bond energy, kJ/mole
Si – O (in Si – O – Si)	443
Pb – O (in Pb – O – Pb)	310
Pb^{2+} – O	151

According to the data in [10], the Si – O bond predominates in the structure of glass with 25% PbO (TF-1), and the number of bonds with low energy (Pb^{2+} – O), where rupture is most probable, is the smallest among the glasses investigated. For this reason, TF-1 glass theoretically has the minimum conditions for $O^{2-} \rightleftarrows N^{3-}$ mutual diffusion. Actually, the diffusion coefficient of oxygen and nitrogen in TF-1 glass has the lowest values.

TF-10 glass contains the maximum amount of PbO, 40%. Some of the lead ions are bound in the glass forming skeleton (Pb – O – Pb) and form a much lower potential barrier for the diffusion jump than the silicon ions in the Si – O – Si bond. In addition, the number of Pb^{2+} – O ionic bonds is higher in the structure of TF-10 glass than in TF-1 glass [11], which also favors diffusion processes, and as a consequence, $D_{\text{TF-10}} > D_{\text{TF-1}}$.

Another important factor in diffusion is the state of the anionic matrix of the glass. We know [12] that quartz glass has the highest gas permeability, which is a function of the free volume of the glass-forming network. When modifiers are introduced in the glass, the vacancies in the structural network are filled and the gas permeability decreases. In glass containing modifiers, the fraction of geometric free

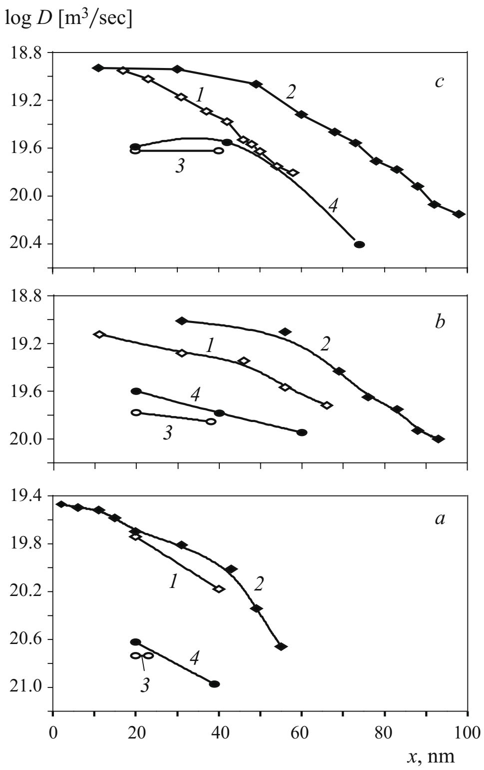

Fig. 2. Diffusion coefficients of oxygen and nitrogen in lead-silicate glasses TF-1 (*a*), TF-5 (*b*), and TF-10 (*c*) after gas heat nitration at a temperature of 425°C and pressure of 1 MPa: *1* and *2*) diffusion coefficient of oxygen in the glass after nitration for 5 and 20 h; *3* and *4*) diffusion coefficient of nitrogen in the glass after nitration for 5 and 20 h.

volume is related to the deformation of the glass network: the larger the cation, the more strongly it will distort and expand the network and the greater its free volume (and thus gas permeability) will be. The gas permeability is due to the presence of cations of large radius in the investigated glass ($r_{Pb^{2+}}$ = 0.12 nm).

The increase in the diffusion coefficient in going from glass with a 25% PbO content (TF-1) to glass containing 40% PbO (TF-10) is probably due to the fact that some of the lead ions in TF-10 glass enter the glass-forming skeleton, causing an increase in the free volume [7].

For all glasses investigated, the oxygen diffusion coefficients are higher than the nitrogen diffusion coefficients (see Fig. 2), which is due to the difference in their diffusion parameters — the anion size and charge. These two factors determine how much the jump frequency (diffusion jump) of the diffusing ion (nitrogen) will differ from the jump frequency of the intrinsic ion (oxygen) and the probability that the impurity ion will occupy a vacant site. Since the ionic radius of oxygen (0.140 nm) is slightly smaller than the ionic radius of nitrogen (0.171 nm), in their mutual diffusion, the jump frequency and number of oxygen vacancies filled by nitrogen will be small. In addition, substitution of oxygen by nitrogen takes place in the quantitative ratio of $3O^{2-} : 2N^{3-}$ [5].

The decrease in the nitrogen diffusion rate over the depth of the surface layer of these glasses is probably due to local changes in the anionic matrix of the glass. The entry of the nitrogen ion with a higher coordination number creates a diffusion barrier for further migration of nitrogen into the depths of the glass by causing an increase in the degree of coherence of the structural skeleton of the glass. This is demonstrated by the very insignificant increase in the diffusion coefficient with a significant (by four times) increase in the duration of the gas heat treatment.

Gas heat treatment of lead-silicate glass with nitrogen at 425°C and pressure of 1 MPa for 5 – 20 h thus modifies the surface layer; mutual anion diffusion between oxygen and nitrogen takes place. Using Auger spectroscopic data, the diffusion coefficients of oxygen and nitrogen were determined: from – 18.95 to – 20.66 and from – 19.18 to – 20.97 [m²/sec], respectively. It was found that the diffusion coefficients are a function of the parameters of the gas heat treatment and the chemical composition of the glass.

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